

Implementation and Validation of the Lacks-Gordon Exchange Functional in Conventional Density Functional and Adiabatic Connection Methods

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ABSTRACT: We present an analysis of the numerical performances of the exchange functional proposed by Lacks and Gordon, which we have implemented in the Gaussian series of programs. This functional has been built with the double aim of respecting most of the known scaling and asymptotic properties and of giving good numerical performances, especially as concerns noncovalent interactions. We have found that the coupling of the Lacks-Gordon exchange and Lee-Yang-Parr correlation functionals provides a reliable conventional density functional approach. The corresponding parameter-free adiabatic connection model, in which the ratio between Hartree-Fock and Lacks-Gordon exchange is determined a priori from purely theoretical considerations, allows us to obtain remarkable results for both covalent and noncovalent interactions in a satisfactory theoretical scheme, encompassing the free electron gas limit and most of the known scaling conditions. © 1998 John Wiley & Sons, Inc. *J Comput Chem* 19: 418–429, 1998

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Introduction

Computational models rooted in the density functional (DF) theory¹ are becoming valuable alternatives to conventional Hartree-Fock (HF) and post-HF methods for the study of molecular electronic structure.² The appeal of these methods is due to their capacity (at least in principle) of taking into full account many-body effects with computer times characteristic of mean field approximations. Unfortunately, the exact density functional is unknown, and approximate functionals must be used. Therefore, a major target in DF approaches has been the development of a general functional for exchange and correlation. In that the magnitude of the correlation energy is generally less than 10% of the exchange energy, it is most important that the exchange functional be accurate. Furthermore, the available correlation functionals already provide satisfactory numerical results for a wide range of chemical problems.³

The simplest DF approach to the exchange energy is the local spin density approximation (LSD), in which the functional for the uniform electron gas of density $\rho(r)$ is integrated over the whole space⁴:

$$E_X^{LSD} = A_x \sum_{\sigma} \int \rho_{\sigma}(r)^{4/3} dr \quad (1)$$

where

$$A_x = -\frac{3}{2} \left(\frac{3}{4\pi} \right)^{1/3} \quad (2)$$

and the index σ denotes either α or β electron spin. Such an approach underestimates the exchange energy by about 10% (see, for instance, Becke⁵). Starting from equation (1), several corrections for the nonuniformity of atomic and molecular densities have been proposed.⁶ In particular, those based on nonlocal density gradients have received considerable attention owing to their simplicity. These corrections, collectively referred to as *generalized gradient approximation* (GGA), are usually expressed in terms of an enhancement factor over the exchange energy of the uniform electron gas, so that the total exchange energy takes the form

$$E_X^{GGA} = E_X^{LSD} - \sum_{\sigma} \int F[x_{\sigma}] \rho_{\sigma}(r)^{4/3} dr \quad (3)$$

where x_{σ} is the dimensionless reduced gradient for spin σ :

$$x = \frac{|\nabla \rho_{\sigma}|}{(\rho_{\sigma})^{4/3}}. \quad (4)$$

A number of semiempirical GGA exchange functionals, which contain parameters obtained by fitting the exchange atomic energies, have been proposed.^{5,6-18} Roughly speaking, these functionals can be divided in two main classes. For the first class, we may group those that can be considered as modifications of the functional proposed by Becke in 1988 (hereafter referred to simply as B),⁹ whose enhancement factor can be expressed as

$$F[x] = \frac{bx^2}{1 + 6bx \sinh^{-1} x} \quad (5)$$

where $b = 0.0042$. In this class, we include the functional developed by Perdew and Wang in 1991 (hereafter called PW),¹⁰ the so-called CAM family of functionals,¹⁷ and the exchange functional of Chermette and coworkers.¹⁴

The other class contains all the functionals that can be expressed as rational functions of the reduced density gradient. Among them, we can mention those introduced by Becke in 1986 (B86),⁷ by Perdew and Wang in 1986 (P),⁸ by Gill (either in its original form¹⁵ or in the modified form proposed by Handy¹⁸), and the very recent functional of Perdew, Burke, and Ernzerhof.¹⁶ For instance, the enhancement factor of the P functional is:

$$F^P[s] = [1 + a_2 s^2 + a_4 s^4 + a_6 s^6]^{1/15} \quad (6)$$

where

$$s = \frac{1}{2(3\pi^2)^{1/3}} x \quad (7)$$

and $a_2 = 1.296$, $a_4 = 14$, $a_6 = 0.2$. All these functionals generally provide atomic or molecular properties with a reasonable precision, so that current GGA methods are claimed to deliver results comparable to those obtained by second-order many-body perturbation approaches (MP2).² From a purely formal point of view, the reason for such good performances is not yet evident. In particular, a number of physical conditions that must be satisfied by an exact exchange functional have been established, but only few of the expressions mentioned above obey them. Among others, three

conditions are of particular importance. The first constraint is related to the behavior in the small x region, where the GGA exchange functional should reduce to E_X^{LSD} in order to recover the correct uniform gas limit.¹⁹ The second condition was defined by Levy and Perdew,²⁰ who showed that some scaling properties can be satisfied if the asymptotic form of the functional for large x is $x^{-\alpha}$, where $\alpha \geq 1/2$. The last condition is the so-called Lieb-Oxford bound,²¹ which, in its "global" version,¹¹ states that

$$E_X \geq E_{XC} \geq -1.679 A_x \int \rho(r)^{4/3} dr. \quad (8)$$

The B functional does not obey either the Levy condition or the Lieb-Oxford bound, but its numerical performances are better than those provided by the PW functional, which respects all the above-mentioned constraints.⁹ This situation is, of course, quite disturbing, and some efforts have been made to design an exchange functional that

couples a rigorous theoretical formalism with good numerical performances. In particular, we have recently proposed a modified version of the PW exchange functional, which leads to improved numerical results, retaining the same parameters and correct physical behavior of the original model.²² We have also found that the correct asymptotic conditions are less important in the high-density (which corresponds to covalent bonds) than in the low-density region. This point is of particular chemical importance; these latter regions are responsible for noncovalent interactions, such as H-bond, van der Waals (vdW), and charge transfer (CT).

In the same vein, some years ago Lacks and Gordon¹¹ proposed an exchange functional (hereafter referred to as LG), built to reproduce correctly the exchange energy of vdW dimers, such as He₂ and Ne₂, while respecting most of the known asymptotic and scaling requirements. The enhancement factor of the LG functional is

$$F[s] = \frac{\left(1 + \frac{a_d + 0.1234}{b}s^2 + a_4s^4 + a_6s^6 + a_8s^8 + a_{10}s^{10} + a_{12}s^{12}\right)^b}{1 + a_d s^2} \quad (9)$$

where $a_4 = 29.790$, $a_6 = 22.417$, $a_8 = 12.119$, $a_{10} = 1,570.1$, $a_{12} = 55.944$, $b = 0.024974$, and $a_d = 1.0 \cdot 10^{-8}$. These parameters were obtained by a weighted least-squares fit to the total energies of He, Ne, and C⁴⁺, the HF differential exchange energy for He and Ne dimers (i.e., the exchange energy of the atom pair minus the exchange energy of the two free atoms), and the first-principle value for the exchange functional derived by Perdew for $s = 0.5$.⁸ These three sets of data allow us to take into account different regions of electron density: The first-principle data point determines the functional at small s , atomic total energies fix the functional at intermediate s , and the noble-gas dimers drive the form of the functional at large s . Furthermore, the LG functional reduces to the gradient expansion for small density gradients and satisfies the Levy scaling inequalities for large density gradients. Despite the accurate procedure used in its derivation, to the best of our knowledge the LG exchange functional has been used so far only in a comparative study of two simple molecules

(CO and N₂O) by several functionals.²³ Therefore, we have thought interesting to embody this functional in a fully self-consistent DF scheme to verify its numerical performances.

From another point of view, it is now well established that self-consistent hybrids (SCHs) of HF and GGA models²⁴ provide a significant improvement over conventional DF approaches.^{24–27} In the original paper by Becke,²⁴ the ratio between HF and DF exchange was taken to be 1 : 1, leading to the so-called half-and-half approach.²⁴ Later, the weight of HF exchange was drastically reduced and three parameter functionals were introduced, in which 20% of HF is mixed with 80% of LSD exchange functional. At the same time the gradient correction to exchange and the local correlation contribution are scaled by 0.72 and 0.81, respectively.²⁴ The mixing and scaling coefficients have been determined by a fitting procedure to thermochemical data. A variant of such an approach, the so-called B3LYP model, leads to quite impressive numerical results for a number of different chemi-

cal situations.^{25–27} Unfortunately some problems arise for those systems in which weak noncovalent interactions play a dominant role.^{28–30}

More recently Becke³¹ has shown that reduction of the number of optimized parameters to one does not worsen the results significantly. From a more fundamental point of view, Perdew and co-workers³² have suggested that the optimal value ruling the exact/DF exchange ratio can be determined by the lowest order of the Gorling-Levy perturbation theory, which provides an accurate description of the energy on the coupling parameter λ in the adiabatic connection integral. Because fourth-order perturbation theory usually delivers very accurate results for molecular systems, we argued that a true adiabatic connection method (i.e., not involving parameters optimized on experimental data) can be expressed as^{3,22}

$$E_{xc}^{ACM} = \frac{1}{4}E_x^{HF} + \frac{3}{4}(E_x^{LSD} + \Delta E_X^{GGA}) + E_c^{LSD} + \Delta E_c^{GGA}. \quad (10)$$

Although the LYP correlation functional does not respect the free-electron gas limit, by using the approximation

$$\Delta E_c^{LYP} = E_c^{LYP} - E_c^{LSD}, \quad (11)$$

a similar equation is formally obtained also in this case.

In particular, we have found that the protocol containing the B exchange functional and the LYP correlation functional (referred to as B1LYP³) performs as well as the parent B3LYP method. Unfortunately, also all the limits of the parent protocol are preserved. These limitations may be due to the noncorrect long-range behavior of the B exchange. To overcome all these problems, we have embodied a functional with correct long-range behavior, i.e., the LG functional, in this protocol. To validate this approach, we have performed a number of electronic computations on a subset of the G2 molecular data set,³³ including all neutral molecules with only first-row atoms plus H₂. This subset is considered as a standard benchmark to verify any DF computational protocol.³⁴ Some “difficult” chemical systems have been chosen to explore the domain of such an approach. In particular, we have considered the estimation of the strength of noncovalent interactions, such as H-bond interaction in different conformers of glycine and a CT complex, the ethylene-Cl₂ adduct. Furthermore, two representative organic reactions, a

proton transfer (PT) process and a S_N2 mechanism, have been investigated. All these systems have been recently shown to be on the borderline of the applicability of DF methods.^{29,35–37}

Computational Method

All the DFT computations are based on the Kohn-Sham (KS) approach to the DF method¹ as implemented in the development version of the Gaussian package.³⁸ In this particular implementation, the exchange-correlation contribution to the total electronic energy is evaluated using a self-consistent procedure that avoids the evaluation of the Hessians of the electronic density.³⁹ As a consequence, the cost of the exchange-correlation part of the electronic calculation scales linearly with the size of the atomic basis set used in the expansion of the molecular orbitals.⁴⁰ Of course, evaluation of the Hessian of electron density cannot be avoided when computing analytical gradients or second derivatives. This task, however, is performed only once in each optimization step. We have added the LG exchange functional to those already available in the Gaussian package. Our implementation includes first and second derivatives with respect to the total electronic density. The analytical expression of the functional, together with the corresponding expressions of first derivative are reported in appendix A.

For purposes of comparison, some computations have also been performed with the standard B exchange functional.⁹ We have used only the functional introduced by Lee, Yang, and Parr⁴² (LYP) for the correlation term, because several studies have confirmed its reliability.^{3,12,41} Using LG and LYP functionals in equation (10), we obtain the LG1LYP model, which can be written as

$$E_{xc}^{LG1LYP} = \frac{1}{4}E_x^{HF} + \frac{3}{4}(E_x^{LSD} + \Delta E_X^{LG}) + E_c^{LYP}. \quad (11)$$

The 6-311G(d,p) basis set of Pople and coworkers⁴³ has been used to optimize all the molecular geometries; previous experience showed that this basis set generally provides nearly converged structural parameters by DF methods.^{36,44} Diffuse functions on heavy atoms have been added for anionic species. An extended basis set, namely, the 6-311++G(3df,3pd) basis set⁴⁵ was used next to evaluate all the energetic parameters (atomization and dissociation energies) and electronic proper-

ties (dipole moments) at the above-mentioned geometries.

Results and Discussion

THE G2 DATA SET

Tables I–III report the LGLYP and LG1LYP results obtained for the geometric and thermodynamic parameters of 32 molecules belonging to the G2 reduced data set. Notice that some of the experimental geometries quoted in the original G2 work³⁴ are quite out of date and have been replaced by the more recent values, critically discussed by Laming et al.¹² On this set of covalently bonded molecules the LG1LYP approach gives results close to those obtained with the B1LYP method,³ for both geometries and atomization energies. Table IV collects a summary of the results obtained for the reduced G2 data set, together with the error statics for the most common DF and post-HF methods. The data reported in this table are sufficiently self-explanatory, so we add only a few comments. The first concerns the LGLYP protocol, which provides geometries with an average error equal to that obtained by the BLYP model, with atomization energies slightly better. As expected, a significant improvement is obtained

TABLE I. Theoretical and Experimental Geometries of the Biatomic Molecules in the Reduced G2 Data Set.^a

Molecule	Parameter	LGLYP	LG1LYP	Exp. ^b
H ₂	r(HH)	0.748	0.743	0.741
LiH	r(LiH)	1.594	1.587	1.595
BeH	r(BeH)	1.394	1.338	1.343
CH	r(CH)	1.138	1.125	1.120
NH	r(NH)	1.055	1.042	1.045
OH	r(OH)	0.988	0.974	0.971
FH	r(FH)	0.933	0.920	0.917
Li ₂	r(LiLi)	2.683	2.682	2.67
LiF	r(LiF)	1.566	1.555	1.564
CN	r(CN)	1.179	1.164	1.172
CO	r(CO)	1.140	1.126	1.128
N ₂	r(NN)	1.109	1.095	1.098
NO	r(NO)	1.168	1.148	1.151
O ₂	r(OO)	1.236	1.205	1.207
F ₂	r(FF)	1.463	1.414	1.417

^aBond distances in Å, bond and dihedral angles in degrees. All theoretical values were obtained with the 6-311G(d,p) basis set.
^bFrom reference 34.

TABLE II. Theoretical and Experimental Geometries of the Polyatomic Molecules in the Reduced G2 Data Set.^a

Molecule	Parameter	LGLYP	LG1LYP	Exp. ^b
CH ₂ (³ B ₁)	r(CH)	1.086	1.079	1.075 ^c
	a(HCH)	135.4	134.8	133.9
CH ₂ (¹ A ₁)	r(CH)	1.125	1.113	1.107 ^c
	a(HCH)	100.1	101.3	102.4
CH ₃	r(CH)	1.086	1.079	1.079
CH ₄	r(CH)	1.098	1.090	1.086
NH ₂	r(NH)	1.042	1.030	1.024
NH ₃	a(NHN)	101.2	102.2	103.4
	r(NH)	1.026	1.015	1.012
	a(HNH)	105.3	106.5	106.0
OH ₂	r(OH)	0.974	0.962	0.957 ^c
	a(HOH)	102.7	103.7	104.5
HCCH	r(CC)	1.208	1.197	1.203 ^c
	r(CH)	1.068	1.062	1.061
H ₂ CCH ₂	r(CC)	1.337	1.327	1.334 ^c
	r(CH)	1.092	1.084	1.081
	a(HCH)	116.3	116.5	117.4
H ₃ CCH ₃	r(CC)	1.531	1.520	1.526
	r(CH)	1.103	1.095	1.088
	a(HCH)	108.3	108.3	107.4
HCN	r(CN)	1.161	1.148	1.153
	r(CH)	1.073	1.065	1.065
HCO	r(CO)	1.189	1.174	1.175 ^c
	r(CH)	1.140	1.126	1.122
	a(HCO)	123.4	124.2	124.6
H ₂ CO	r(CO)	1.213	1.200	1.208 ^c
	r(CH)	1.120	1.109	1.116
	a(HCH)	115.0	115.4	116.5
H ₃ COH	r(CO)	1.444	1.423	1.421
	r(CH _a)	1.098	1.091	1.093
	r(CH _b)	1.107	1.098	1.093
	r(OH)	0.973	0.961	0.963
	a(OCH _a)	106.8	106.9	107.0
	a(COH)	108.1	107.7	108.0
H ₂ NNH ₂	a(HbCH _b)	108.5	108.6	108.5
	r(NN)	1.468	1.438	1.447
	r(NH _b)	1.023	1.014	1.008
	r(NH _a)	1.023	1.014	1.008
	a(NNH _b)	109.0	109.5	109.2
	a(NNH _a)	109.0	109.5	109.2
HOOH	a(H _a NNH _b)	112.9	113.4	113.3
	d(H _a NNH _b)	86.4	87.7	88.9
	r(OO)	1.509	1.457	1.475
	r(OH)	0.979	0.965	0.950
	a(OOH)	98.5	96.7	94.8
	d(HOOH)	122.7	120.0	120.0
CO ₂	r(CO)	1.176	1.159	1.160 ^c

^aBond distances in Å, valence and dihedral angles in degrees. All theoretical values were obtained with the 6-311G(d,p) basis set.
^bFrom reference 34 unless otherwise indicated.
^cFrom reference 17.

TABLE III.
Theoretical and Experimental Atomization Energies (kJ/mol) of 32 Molecules in the Reduced G2 Data Set.^a

Molecule	LGLYP	LG1LYP	Exp. ^b
H ₂	429.7	428.0	432.2
LiH	241.0	236.0	234.3
BeH	228.9	228.4	196.2
CH	349.8	343.1	334.3
CH ₂ (³ B ₁)	752.3	750.6	751.4
CH ₂ (¹ A ₁)	720.5	710.0	713.8
CH ₃	1,212.9	1,208.3	1,210.0
CH ₄	1,633.4	1,626.3	1,642.2
NH	367.8	342.7	330.5
NH ₂	761.1	734.3	711.3
NH ₃	1,187.0	1,156.5	1,157.7
OH	441.4	423.8	423.8
OH ₂	919.2	890.4	917.6
FH	563.2	543.5	565.7
Li ₂	95.4	87.9	100.4
LiF	592.5	561.5	575.7
HCCH	1,645.1	1,605.0	1,627.2
H ₂ CCH ₂	2,229.7	2,202.5	2,225.5
H ₃ CCH ₃	2,750.6	2,737.2	2,787.8
CN	817.6	737.6	738.9
HCN	1,327.2	1,264.4	1,262.7
CO	1,096.2	1,044.7	1,071.9
HCO	1,181.1	1,124.2	1,130.9
H ₂ CO	1,459.8	1,472.8	1,494.5
H ₃ COH	2,010.8	1,973.6	2,011.7
N ₂	1,030.5	949.8	941.8
H ₂ NNH ₂	1,762.7	1,695.4	1,696.2
NO	707.9	628.9	628.0
O ₂	562.3	483.3	493.7
HOOH	1,090.4	1,011.3	1,055.6
F ₂	193.7	119.2	154.4
CO ₂	1,660.6	1,564.8	1,597.9

^aTheoretical values were obtained using 6-311 + + G(3df,3pd) basis set with 6-311G(d,p) geometries and including ZPE corrections.

^bFrom reference 34.

using the LG1LYP model, whose mean absolute deviation for the geometrical parameters and atomization energies are 0.005 Å and 3.6 kcal/mol, respectively. In this respect a particularly significant comparison is that to the results obtained by the B1LYP approach, our parameter-free ACM protocol, which performs, over the G2 data set, nearly as well as the popular B3LYP method (see Table IV). This analysis shows that the performances of the two models are very close to each other, with the B1LYP results only marginally better than those obtained with the LG1LYP protocol.

TABLE IV.
Mean Absolute Deviations Obtained by Different Methods for Some Properties of 32 Molecules in the Reduced G2 Data Set.^a

Method	Bond lengths (Å)	D ₀ (kJ mol ⁻¹)	Dip. mom. (D)	Harm. freq. (cm ⁻¹)
HF ^{b,c}	0.022	340	0.29	144
MP2 ^{c,d}	0.014	100	0.28	99
CCSD[T] ^{b,e}	0.005	46	0.10	31
LDA ^{b,e}	0.017	180	(0.25) ^{c,d}	(75) ^{c,d}
BLYP	0.013	42	0.10	59
LGLYP	0.013	30	0.10	60
B1LYP	0.004	12	0.08	33
LG1LYP	0.005	16	0.07	38
B3PW91	0.008	20	0.08	45
B3LYP	0.004	10	0.08	31

^aBond lengths, bond angles, and harmonic frequencies were computed using the 6-311G(d,p) basis; atomization energies and dipole moments were evaluated by the 6-311 + + G(3df,3pd) extended basis set.

^bBasis set of triple- ζ quality + double polarization func.

^cReference 34.

^d6-31G(d,p) basis set.

^eReference 17.

NONCOVALENT INTERACTIONS

The results described above, together with several other computations performed in our laboratory, convinced us that LG is a reliable exchange functional for covalently bonded molecules. On the other hand, it is true that the molecular parameters of the above-mentioned G2 molecules are relatively well described by all the most common quantum mechanical methods. The situation is more involved as concerns noncovalent interactions, such as those present in H-bond or CT complexes, where a wide range of results is obtained with different DF methods. Therefore, to have a better appraisal of the field of applicability of the LG functional, we have chosen two systems that may be considered as prototypes to analyze these weak interactions, namely, glycine and the CT complex formed by Cl₂ with C₂H₄.

Let us start from glycine, whose conformational behavior is ruled by subtle effects. In particular, the overwhelming role of correlation in determining the relative stabilities of the different isomers imposes the use of the most sophisticated computational techniques.^{35,46-49} As a consequence, glycine has been used as a particularly demanding benchmark for assessing the quality of different

quantum mechanical approaches.^{35,49} Among the several energy minima located at different values of torsional angles, we have focussed our attention on the two most stable conformers (see Fig. 1). Geometrical parameters obtained by a number of

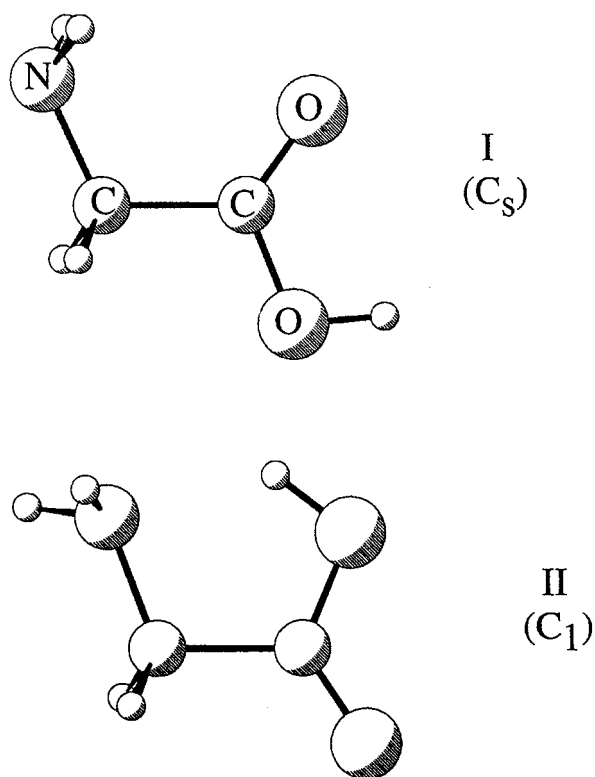


FIGURE 1. Structure of the glycine conformers examined in this study.

computational models^{46,47,49} are collected in Table V, together with the available experimental data.⁵⁰ All the results provided by pure DF approaches, including those obtained by the recent BLAP1 and PLAP1 protocols of Salahub and coworkers,⁵¹ are close to each other. In particular, the CC and C=O bond lengths are overestimated by 0.01 Å, while the C—O bond is predicted to be 0.02 Å longer than the experimental value. In contrast, the NC bond length is underestimated by 0.01 Å. On the other hand, the results obtained by the two ACM methods considered, namely, B1LYP and LG1LYP, are very close to the CCSD results and in fairly good agreement with the experimental findings. Comparable results are obtained by three-parameter protocols, such as B3LYP (see Table V and Barone et al.³⁵).

The relative energies of the two conformers considered are plotted in Figure 2. Standard DF methods, such as BLYP, predict a vanishing energy difference between the two lowest conformers. The LGLYP approach induces a small, but significant, improvement over the BLYP value, reaching an energy difference very close to that obtained by the B3LYP protocol.³⁵ An even better result ($\Delta E = 5.0 \text{ kJ mol}^{-1}$) is obtained at the LG1LYP level. The experimental estimate is $6 \pm 2 \text{ kJ mol}^{-1}$.⁵² Also, recent methods using the LAP1 correlation functional⁵¹ provide reliable results, but this is at the expense of quite poor geometries.

A final remark must be added on the BLYP and B3LYP values (plotted in Fig. 2), obtained with the 6-311 + + G(3df,3pd) extended basis set. These

TABLE V. Comparison of the Optimized Geometrical Parameters (Å and Degrees) of the Most Stable Conformers of Glycine, Obtained Using the 6-311G(d,p) Basis Set.

	MP2 ^a	CCSD ^b	BLYP	BLAP1 ^c	PLAP1 ^c	LGLYP	B1LYP	LG1LYP	B3LYP	Exp. ^d
CC	1.519	1.525	1.539	1.536	1.538	1.540	1.523	1.525	1.524	1.526
NC	1.447	1.458	1.464	1.453	1.457	1.469	1.451	1.453	1.451	1.467
C—O	1.356	1.359	1.374	1.372	1.379	1.378	1.352	1.355	1.354	1.355
C=O	1.209	1.216	1.216	1.217	1.219	1.218	1.203	1.204	1.204	1.205
OH	0.968	0.972	0.986	0.971	0.973	0.981	0.967	0.968	0.969	
CH	1.094	1.098	1.101	1.087	1.088	1.102	1.094	1.093	1.095	
NH	1.014	1.021	1.024	1.010	1.011	1.026	1.014	1.015	1.016	
NCC	115.6	115.4	115.7	116.0	116.0	115.6	115.4	115.4	115.4	
CC—O	110.9	111.5	111.3	111.2	111.0	111.1	111.5	111.4	111.5	111.6
CC=O	125.7	125.7	125.6	125.8	125.9	125.6	125.4	125.4	125.4	125.1
COH	0.57	0.56	106.1	106.6	106.7	106.1	107.0	107.0	106.9	

^aTZP basis set; reference 47.

^bDZP basis set; reference 48.

^cDZVP basis set; reference 49.

^dReference 50.

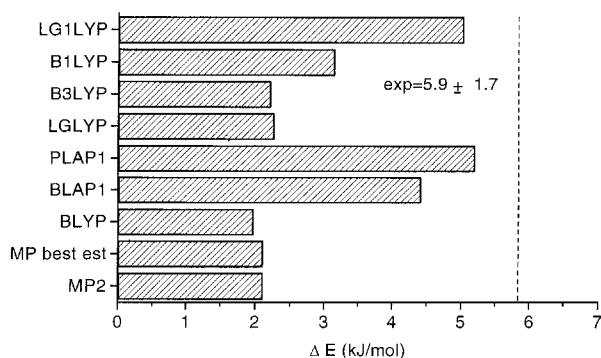


FIGURE 2. Relative stabilities of the conformer II of glycine with respect to conformer I. Values labelled MP2 and MP best are from Lelj et al.⁴⁶

values are significantly higher than the corresponding values that we have reported in our early paper, carried out with smaller basis sets.³⁵ This shows, once again, the relevant role played by the choice of the basis set expansion in determining DF performances, especially as concerns H-bonds.^{28,36} Because the basis set (DZVP)⁵³ used in BLAP1 and PLAP1 computations is far from convergence, we can estimate that these functionals actually overestimate H-bond strengths.

An even more stringent test is represented by CT complexes, and in particular those arising from a π - σ type interaction, such as the ethylene interacting with a halogen molecule. These systems are very difficult to describe either by the post-HF^{54,55} or by the DF^{22,29,56} approaches. In particular, DF and most of the hybrid methods predict intermolecular distances that are too short and interaction energies that are too high.⁵⁶ In the present study, we have focussed our attention on the simple ethylene-chlorine complex. Furthermore, even if several possible molecular rearrangements are possible, the axial-perpendicular struc-

ture is the most stable.⁶ Therefore, we have limited our attention to only this molecular rearrangement, whose main molecular parameters are reported in Table VI. The most significant features of the calculations with the different methods are the chlorine-ethylene distances, which are directly related to the interaction strengths. In this connection, GGA methods provide very short intermolecular distances, with the LGLYP result (2.73 Å) very close to the BLYP value (2.71 Å). The inclusion of some HF exchange increases the distance to 2.89 Å for the LG1LYP model, a value approaching the experimental value (3.13 Å).

The trend in the geometrical parameters is reflected in the harmonic frequencies and, in particular, in the stretching of the Cl-Cl bond. In this complex, the intermolecular distance is directly related to the σ - π electron donation from chlorine to ethylene, which weakens the Cl-Cl bond. As a consequence, any overestimation of this interaction induces a very low Cl-Cl stretching frequency. This is the case for the conventional DF approaches, which predict a harmonic wave number significantly lower than the experimental estimate. The best agreement is found at the LG1LYP level, whose value is close to the MP2 prediction (467 vs. 506 cm^{-1} , respectively), which is, in turn, slightly lower than the experimental value of 527 cm^{-1} .⁵⁸

Table VI also reports the interaction energies, corrected for both ZPE and BSSE⁵⁹ effects (about 4 and 1 kJ mol^{-1} , respectively, for all DF methods). As expected, these energies are functions of the intermolecular distances. Thus, the LGLYP model predicts a strong Cl-C₂H₄ interaction (-12.1 kJ mol^{-1}), which is reduced to -5.4 kJ mol^{-1} at the LG1LYP level. This last value is only slightly lower than the MP2 estimate (-6.7 kJ mol^{-1}) or the experimental findings (between -7.1 and -11.3 kJ mol^{-1}).^{60,61}

TABLE VI.

Some Relevant Geometrical Parameters (Å), Harmonic Stretching Cl-Cl Frequencies (cm^{-1}) and Complexation Energies (kJ mol^{-1}) for the C₂H₄-Cl₂ Complex.^a

	MP2 ^b	BLYP	LGLYP	B1LYP	LG1LYP	B3LYP	Exp. ^c
d(Cl-plane)	3.003	2.707	2.728	2.901	2.887	2.903	3.128
d(ClCl)	2.044	2.183	2.203	2.093	2.104	2.091	
v(Cl-Cl)	506	359	362	447	460	440	527
ΔE _{comp}	-6.7	-10.9	-12.1	-4.6	-5.4	-6.3	-7.1 / -11.3

^aThe energies are computed at the 6-311++G(3df,3pd) level, using 6-311G(d,p) geometries, and are corrected for BSSE and ZPE effects.

^bReference 56.

^cReferences 58, 60, 61.

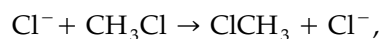
PROTON TRANSFER IN MALONALDEHYDE

Despite its apparent simplicity, the proton transfer (PT) reaction is one of the most difficult processes to describe by quantum chemical procedures, in either the post-HF or the DF frameworks. In particular, several authors have explored the applicability of DF methods to the study of PT processes, showing that standard DF approaches provide very low activation energies.^{28,36,49,61–65} The situation is even more involved when the motion of the proton is coupled with a rearrangement of the π electronic system, as happens in malonaldehyde (Fig. 3). In this case, the underestimation of the PT activation energy by DF methods is augmented by the overestimation of correlation energy, which produces an excessive degree of conjugation in the molecular backbone. In a previous detailed analysis,³⁶ we have estimated the PT barrier to be 18 ± 1 kJ mol⁻¹, using the G2(MP2) approach.⁶⁶ Standard GGA methods provide very low barriers (about 8 kJ mol⁻¹), with the exception of protocols containing the LAP correlation functional.⁵¹ In particular, the BPLAP1 model gives a value (13.8 kJ mol⁻¹) lower than the G2(MP2) estimate, whereas the PLAP1 result is higher (18.8 kJ mol⁻¹).⁴⁹ These results point out the relevant role played by the exchange functional. The B3LYP/6-311 + G(3df,2p) result (12 kJ mol⁻¹) is higher than standard GGA values but significantly lower than the G2(MP2) reference. Table VII reports the results obtained by the LG exchange functional. Already the conventional DF approach (LGLYP) gives a good description of the PT reaction, providing an energy barrier of 15.1 kJ mol⁻¹. A further increase is next obtained at the LG1LYP level, leading to a barrier of 20.5 kJ mol⁻¹. In contrast, the B1LYP value is 15.5 kJ mol⁻¹, confirming the remark made above that the Becke exchange functional tends to underestimate PT

barriers, whereas Perdew-like exchanges (P and LG) tend to overestimate it. As concerns the H-bond geometrical parameters, subtle effects rule the relationship between O–O distance and energy barrier, so that a direct connection between these two factors cannot be drawn. In contrast, the inclusion of HF exchange in the functional induces an increase of the distance between the moving proton and the acceptor oxygen atom, leading to a significant increase of the barrier. This effect is observed both for the BLYP–B1LYP pair (where the distance goes from 1.66 to 1.71 Å) and for the LGLYP–LG1LYP pair (where the distance goes from 1.73 to 1.76 Å).

THE WALDEN INVERSION

As a last significant test, we have chosen an S_N2 reaction, whose importance in organic chemistry is well evidenced by the accumulation of a large body of experimental and theoretical data.^{67–73} From a theoretical point of view, several studies have shown these reactions to be extremely sensitive to the theoretical model used.^{68–70} Already the thermodynamics of the simple Walden inversion,



are difficult to describe by quantum mechanical methods. This is particularly true at the DF level, where all the methods, including the B3LYP protocol, fail in predicting some thermodynamical quantities.⁷⁰

This reaction is characterized, in the gas phase, by a double-well energy profile, with two minima corresponding to the formation of a pre- and postreaction ion–molecule complex (Cl–CH₃Cl) and to the saddle point (SP) with a rearrangement of D_{3h} symmetry (ClCH₃Cl⁻). The most signifi-

TABLE VII.
Main H-Bond Geometrical Parameters (Å) and Relative Energies (kJ mol⁻¹) for the Minimum (M) and Saddle Point (SP) of Malonaldehyde.^a

Parameter	G2(MP2) ^b		BLYP		LGLYP		PLAP1 ^c		BLAP1 ^c		LG1LYP		B1LYP		B3LYP	
	M	SP	M	SP	M	SP	M	SP	M	SP	M	SP	M	SP	M	SP
O–O	2.581	2.355	2.581	2.399	2.631	2.412	2.626	2.394	2.591	2.381	2.625	2.371	2.593	2.363	2.580	2.367
H–O	1.678	1.197	1.656	1.224	1.727	1.232	1.731	1.224	1.684	1.216	1.755	1.212	1.710	1.207	1.686	1.208
OH	0.991	1.197	1.019	1.224	1.010	1.232	1.000	1.224	1.003	1.216	0.988	1.212	0.992	1.207	0.998	1.2088
ΔE	0.0	18.03	0.0	8.8	0.0	15.1	0.0	18.8	0.0	13.8	0.0	20.5	0.0	15.5	0.0	12.6

^aThe relative energies are computed at the 6-311 + + G(3df,3pd) level, using 6-311G(d,p) geometries.

^bReference 36.

^cDZVP basis set; reference 49.

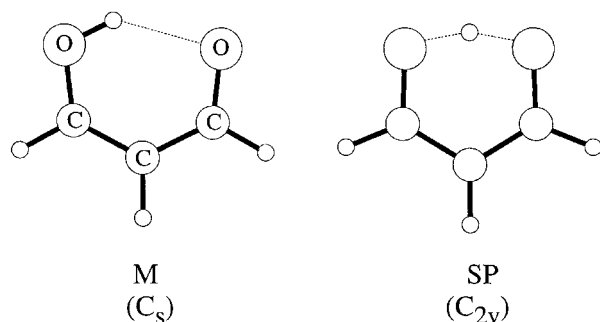


FIGURE 3. Structure of the energy minimum (M) and of the saddle point (SP) of malonaldehyde.

cant thermodynamic quantities are the complexation energies of the ion–molecule complex (ΔE_{comp}); the activation energy, i.e., the relative energy of the D_{3h} SP with respect to the ion–molecule complex ($\Delta E^\#$); and the overall barrier (ΔE_{ovr}), defined as the difference between these two energies. The geometric parameters of the ion–molecule complex and the SP are given in Table VIII, and the corresponding energetic quantities are given in Table IX. The key parameter for understanding the behavior of the different functionals is the distance between the chloride anion and the carbon of the methyl chloride. In this case the MP2 results can be considered as the reference data, the distances being 3.270 Å and 2.317 Å for the ionic complex and for the SP, respectively. The LGLYP model leads to a distance for the ion–molecule complex (3.113 Å) that is too short and a bond length (2.444 Å) for the C–Cl bond in the SP that is too long. This incorrect trend is slightly improved by the LG1LYP protocol, which gives 3.160 and 2.355 Å for the distances in the

TABLE VIII. Main Geometrical Parameters of the Ion Complex Cl[−]–CH₃Cl and the Corresponding Saddle Point for the Walden Inversion.^a

Parameter	MP2 ^b	LGLYP	B1LYP	LG1LYP	B3LYP
Ion complex					
d(C–Cl)	3.270	3.113	3.189	3.168	3.188
d(CCl)	1.810	1.922	1.857	1.862	1.856
d(CH)	1.085	1.088	1.081	1.082	1.086
a(ClCH)	108.8	106.9	107.9	107.8	108.1
Saddle point					
d(CCl)	2.317	2.444	2.373	2.395	2.372
d(CH)	1.073	1.078	1.071	1.071	1.074

^aAll values are computed at the 6-311 + G(d,p) level.

^bReference 71.

TABLE IX. Complexation Energies of the Ion–Molecule Complex (ΔE_{comp}), Activation Energy ($\Delta E^\#$), and Overall Activation Energy Relative to Reactants (ΔE_{ovr}) for the Walden Inversion, Computed at Various Computational Levels.^a

	G2(MP2) ^b	LGLYP ^c	B1LYP ^c	LG1LYP ^c	Exp. ^d
ΔE_{comp}	44.4	48.5	41.0	44.8	51 ± 8
$\Delta E^\#$	54.4	44.4	37.2	37.2	55 ± 8
ΔE_{ovr}	10.5	−4.6	−3.3	−7.5	4 ± 4

^aAll values are in kJ mol^{−1}.

^bReference 71.

^c6-311 + + G(3df,3pd) energies at 6-311G(d,p) geometries.

^dReferences 72, 73.

minimum and SP, respectively. These geometric trends are reflected in the computed energetic parameters. In particular, any increase of the Cl–C distance induces a significant stabilization of the SP structure with respect to the minimum. The effect may be so relevant that it induces a negative value for ΔE_{ovr} . This is true for all the methods considered in the present paper, as well as for all other conventional functionals.⁷⁰ In particular, the B3LYP method predicts an overall barrier of −3.8 kJ mol^{−1}, and, unfortunately, similar trends are observed using the LG1LYP (−7.5 kJ mol^{−1}) and B1LYP (−3.3 kJ mol^{−1}) models.

Conclusions

The development and testing of new functionals has recently received a strong impetus from the availability of more sophisticated models retaining the very favorable scaling of all DF-based methods with the number of electrons. In this framework, most of the work has been devoted to regions of high electron density. By contrast, the exchange functional proposed by Lacks and Gordon also takes care of low-density high-gradient regions, which are important for noncovalent interactions. A fully self-consistent implementation of this functional both in conventional and in hybrid density functional models gives satisfactory results for a number of physicochemical properties.

The remaining shortcomings seem to be related to the correlation rather than to the exchange part of the overall functional. In particular, the medium- and long-range behavior of current correlation functionals could be worthy of deeper investigations, in order to improve the behavior of density functional methods in these regions. Also with this

remark in mind, the LG1LYP model seems a reliable, robust, and theoretically sound tool for the study of large systems.

Acknowledgments

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Appendix

The LG gradient corrected exchange functional has the form given in eq. (9). The relevant first derivatives are:

$$\frac{\partial F}{\partial \rho_\sigma} = \frac{4}{3} [F(s) - xF'(s)] \quad (\text{A.1})$$

$$\frac{\partial F}{\partial \nabla \rho_\sigma} = \frac{1}{2} \Delta \rho_\sigma^{-1/2} F(s) \quad (\text{A.2})$$

$$F'(s) = \frac{b}{(1 + a_d s^2)} \left(\frac{2(0.1234 + a_d)s}{b} + 4a_4 s^3 + 6a_6 s^5 + 8a_8 s^7 + 10a_{10} s^9 + 12a_{12} s^{11} \right) \left(1 + \frac{(0.1234 + a_d)s^2}{b} + 4a_4 s^4 + 6a_6 s^6 + 8a_8 s^8 + 10a_{10} s^{10} + 12a_{12} s^{12} \right)^{b-1} - \frac{2a_d s}{(1 + a_d s^2)^2} \left(1 + \frac{(0.1234 + a_d)s^2}{b} + 4a_4 s^4 + 6a_6 s^6 + 8a_8 s^8 + 10a_{10} s^{10} + 12a_{12} s^{12} \right)^b \quad (\text{A.3})$$

where s , defined in eq. (7), can refer either to α or to β spin.

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